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**CHEMOVISCOSITY MODELING FOR THERMOSETTING RESIN
SYSTEMS - III**

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FOREWORD

This work was supported by the Polymeric Materials Branch (PMB), Langley Research Center, under Contract NAS1-18000 and Grant NAG1-569. This is a progress report on an ongoing research project toward the chemoviscosity modeling for reactive resin systems, and was monitored by R. M. Baucom of PMB. Two earlier reports concerning the same subject matter were:

1. Chemoviscosity Modeling For Thermosetting Resins - I, NASA CR - 172443, November, 1984.
2. Chemoviscosity Modeling For Thermosetting Resins - II, NASA CR - 177958, August, 1985.

This work will also appear in SAMPE Journal, November, 1988.

ABSTRACT

A new analytical model for simulating chemoviscosity of thermosetting resin has been formulated. The model is developed by modifying the well established Williams-Landel-Ferry (WLF) theory in polymer rheology for the thermoplastic materials. By introducing a relationship between the glass transition temperature $T_g(t)$ and the degree of cure $\alpha(t)$ of the resin system under cure, the WLF theory can be modified to account for the factor of reaction time. Temperature-dependent functions of the modified WLF theory parameters $C_1(T)$ and $C_2(T)$ were determined from the isothermal cure data. Theoretical predictions of the model for the resin under dynamic heating cure cycles were shown to compare favorably with the experimental data. This work represents a progress toward establishing a chemoviscosity model which is capable of not only describing viscosity profiles accurately under various cure cycles, but also correlating viscosity data to the changes of physical properties associated with the structural transformations of the thermosetting resin systems during cure.

Key Words:

Chemoviscosity, Modeling, WLF equation, Degree of Cure.

INTRODUCTION

Perhaps the single most important property of a polymer with regard to specifying its processing characteristics is its viscosity. Viscosity governs the resin flow characteristics. For thermoplastic materials, the viscosity is influenced by local flow geometry and can vary with processing temperature and shear rate. Viscosity control becomes more critical and difficult in the processing of thermosetting resins, because of the onset of chemical reactions and the generation of heat during cure which causes the viscosity to vary with time.

In a typical autoclave operation for the fabrication of composite materials, the viscosity-time profile must allow first for the bubbling off of trapped gas, then fiber compaction with resin flow, and finally, laminate consolidation under applied pressure before the resin has gelled and ceases to flow [1]. At the start of a cure cycle (temperature profile), the polymerization reaction begins and the polymers chains lengthen. The increase in viscosity of the resin due to polymerization reaction is, however, largely offset by the increase in temperature, which is introduced through the cure cycle, and the heat of reaction. Consequently, a drop in resin viscosity of two or three orders of magnitude at the initial stage of cure is not uncommon. As the resin continues to polymerize, crosslinks are formed and the viscosity of the resin system starts to increase at a faster rate. Finally, the rate of increase of viscosity approaches infinity at gelation. Therefore, any chemoviscosity profile is closely related to the reaction kinetics of the resin systems and the cure cycle during processing. A fundamental understanding of the chemoviscosity kinetics of thermosetting resin is necessary in order to obtain a precise processing control.

In this study, the thermal and rheological measurements on a neat resin system were conducted by means of differential scanning calorimetry and rheometry, respectively. A well-established viscosity-temperature relationship in polymer rheology is introduced and an analytical model for chemoviscosity profile of the thermosetting resin during cure is formulated. Comparisons between the model predictions and experimental chemoviscosity profiles under both isothermal and dynamic heating conditions are also presented.

THEORETICAL

Numerous researchers have devoted considerable efforts to establish an analytical model for the chemoviscosity growth profile of thermosetting resins during cure. There are two different basic approaches to this subject. The most common approach to the problem has been by empirically specifying the viscosity linearly as an exponential function of reaction time [2,3], or with the aid of DSC thermal analysis, the degree of cure [4,5].

The empirical model proposed by Roller [3] to correlate isothermal viscosity data for a curing B-staged epoxy resin can be expressed as

$$\ln \eta = \ln \eta_0 + k t \quad (1)$$

where η is the time dependent viscosity, η_0 is the zero-time viscosity, k is an apparent kinetic factor, and t is the curing time. The temperature dependences of the parameters η_0 and k are formulated with Arrhenius expressions. In case of dynamic heating where the cure cycle is a function of time, the chemoviscosities are then modeled by numerical integrations of Eq. (1) with respected to curing times.

By comparing the calculated viscosity in Eq. (1) to the experimental values, Roller [3] noted that there exists a large discrepancy, especially in the higher heating rate cases. It seemed that such empirical simulation of chemoviscosity is inadequate in accurately describing the non-linearity of the chemoviscosity-time profile associated with the advancement of resin under dynamic heating in the cure cycle. The model is also found to be very much batch-specific and cannot be related directly to the resin chemistry.

The second approach [1,6,7,8,9] is based on a modification to the well-established viscosity-temperature relationship existing in polymer rheology for thermoplastic materials. The parameters in such an equation can be expressed in terms of polymerization kinetics, and the chemoviscosity profiles as a function of reaction time can then be modeled for thermosetting resin system.

The Williams-Landel-Ferry (WLF) theory [10] states that for $T_g < T < (T_g + 100 \text{ }^\circ\text{K})$, the temperature-dependent viscosity of the polymeric material can be given by the expression

$$\log \left(\frac{\eta_T}{\eta_{T_g}} \right) = - \frac{C_1 (T - T_g)}{C_2 + T - T_g} \quad (2)$$

where C_1 and C_2 are material parameters. Values of C_1 and C_2 were thought initially to be universal constants. It was later found that they were actually material dependent[11]. The temperature dependency of the viscosity indicated in Eq. (2) has been tested and found valid for materials ranging from dilute polymeric liquids and thermoplastic melts, to rubbers and elastomers. Equation (2) can be derived from the semi-empirical Doolittle equation which relates the viscosity to the free volume of the liquid.

The normal use of the WLF equation for thermoplastic materials requires the glass transition temperature (T_g) be constant while the temperature (T) is varied for the specific polymer under study. Equation (2) is applicable for a temperature T up to 100 °K higher than the T_g of the material. However, during the cure of thermosetting resins, the monomers are initially polymerized and later crosslinks are formed. This is a system where $T_g(t)$ is changing and the curing temperature, T , is held constant (in the isothermal curing case, for example). The glass transition temperature, T_g , rises continuously and eventually approaches the curing temperature. Over the entire curing cycle, the material structure actually undergoes a continuous phase transformation from the low molecular weight liquid to the high molecular weight polymeric melt, and eventually transforms to form the crosslinking networks. If it is assumed that $T_g(t)$ of the material under cure is always lower than the cure temperature T , and that $(T - T_g(t))$ is always within 100 °K, then the WLF theory should be applicable to all polymer structure phases during the cure. However, before Eq. (2) can be applied to describe the chemoviscosity of the curing resin, modifications have to be made to properly account for the reaction time, t , of the thermosetting resin system.

One method of introducing reaction time factor into the WLF equation is to express the glass transition temperature $T_g(t)$ as a function of $\alpha(t)$, the degree of cure. Several different techniques have been used in literature which include thermal, spectrophotometric (FTIR) and chromatographic (HPLC) measurements to determine the extent of cure. In the present study, we assume that for the resin system under investigation, $\alpha(t)$ at time t is equal to the fraction of heat released, as measured by DSC, up to time t for the resin system under cure. The α 's thus determined are a function of the curing temperature and time. The objective of present study is to investigate, through the experimentally determined linkage between $T_g(t)$ and $\alpha(t)$ for a given reactive resin system, how well the chemoviscosity could be simulated by the WLF equation, Eq.

(2), which is properly modified as described above. The two material parameters, C_1 and C_2 , in Eq. (2) should be variable with reaction time because of the transformation of different material structures during cure.

EXPERIMENTAL

Material

The material used in this study is Hercules 3501-6 resin system*. This thermosetting resin is selected because of its wide use in aerospace industry. The material received from the manufacturer was used without further treatment, and was kept in dark and cold environments at around -5°C until usage.

This resin system contains the following standard concentrations of starting components [12]:

Component	Percent by wt.
Tetraglycidyl Methylenedianiline	56.5
Alicyclic Diepoxy Carboxylate	9.0
Epoxy Cresol Novalac	8.5
Diaminodiphenyl Sulfone	25.0
Boron Trifluoride Amine Complex	1.1

Thermal Measurement

Thermal properties of the resin system during cure were measured by a Perkin-Elmer Differential Scanning Calorimeter (DSC) model DSC-2. Samples of few milligrams were weighed into aluminum sample holders on an analytical balance to accurate to 10^{-7} kgs. A stream of dry nitrogen was continuously flowing over the sample and the reference during measurements. The glass transition temperatures, T_g , and the heat of reaction, ΔH , were determined directly from the thermograms for the samples cured under either isothermal or dynamic heating conditions. The temperature and energy scales of the machine were calibrated in advance according to the melting points and melting energies of several standard reference compounds as suggested by the manufacturer [13].

*Hercules 3501-6 resin system is manufactured by Hercules Inc.

Chemoviscosity Measurement

A Rheometrics System 4 Rheometer was used for chemoviscosity measurements. The sample was confined in the gap between two parallel plates mounted in the Rheometer. The top plate is motor driven about its axis while the bottom plate is mounted on a torque transducer for force measurement. The typical gap between the parallel plates was .0012 m. The plates and sample are enclosed in a heat chamber where temperature control is provided. Though the shear field in parallel-plate flow geometry is non-uniform, for the small amplitude displacements used, these effects can be safely neglected. Plate oscillatory motion was set at a frequency of 1.59 Hz (10 rad/sec), and an amplitude (strain) equivalent of 1 percent of the gap was used for all measurements reported. Selection of the strain value was to assure that the measurements were performed within the material's linear viscoelastic response range.

It is well known that the viscoelastic properties of polymeric materials respond differently to different frequencies, and selection of the frequency value was made to assure that the complex viscosities measured were within the Newtonian range. The cure mode of the Rheometer was used during testing which automatically programmed different temperature profiles as the epoxy is cured. Both isothermal and dynamic heating measurements were performed.

RESULTS AND DISCUSSION

Determination of Degree of Cure

The measurements of heat of reaction and degree of cure by means of DSC under dynamic heating conditions were performed with four different heating rates, i.e., 10, 20, 40, 80 °K/min. A typical thermogram obtained at 20 °K/min scan is shown in Figure 1. The small hump preceded the major exothermic peak is attributed to the BF₃ catalytic effect [2]. The total heat of reaction, H_T , was calculated by numerical integration (Simpson's rule) of the area under the reaction peaks on the thermogram. The value of H_T is found constant over the four heating rates investigated. An average value of $H_T = 502 \pm 21$ Joules/g was chosen for all further calculations. This value is different from $H_T = 474.4$ Joules/g reported by Lee et al. [4] on the same resin system. This is possibly caused by materials with different aging histories and by the schemes employed in determining thermogram and the area under the reaction peaks of the curve.

The degree of cure, $\alpha(t)$, is defined as the fraction of heat, $H(t)$, released up to time, t , for the resin system under cure:

$$\alpha(t) = H(t)/H_T, \quad (3)$$

The rate of degree of cure can then be expressed by

$$\frac{d\alpha}{dt} = \frac{1}{H_T} \frac{dH}{dt} \quad (4)$$

Values of $\alpha(t)$ for the materials cured by different heating rates are plotted in Figure 2. Open and filled symbols represent measurements from different runs under the same condition. The reproducibility of the measurements appears to be quite satisfactory.

Lee et al. [4] also performed thermal analyses on the same epoxy resin system by the DSC. The degree of cure and the rate of change of degree of cure, as determined by Eqs. (3) and (4), were reported under isothermal curing conditions. Eight different temperatures ranging from 400 to 475 °K were selected. The following equations were found to describe these temperature-dependent quantities rather accurately:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha)(1 - \alpha)(B - \alpha), \quad \alpha \leq 0.3 \quad (5.1)$$

$$\frac{d\alpha}{dt} = k_3 (1 - \alpha), \quad \alpha > 0.3 \quad (5.2)$$

where

$$k_1 = A_1 \exp(-\Delta E_1/RT),$$

$$k_2 = A_2 \exp(-\Delta E_2/RT),$$

$$k_3 = A_3 \exp(-\Delta E_3/RT),$$

with R, the universal gas constant and T, the cure temperature in °K. Values of the constants in Eqs. (5.1) and (5.2) are summarized in Table 1.

Eqs. (5.1) and (5.2) represent two first order nonlinear and initial value differential equations. Assume that $d\alpha/dt$ is sufficiently differentiable with respect to either t or α , one can expand $\alpha(t)$ in a Taylor series about the initial curing time $t = t_0$. The expanded Taylor series was then used as a model to calculate $\alpha(t)$ under various dynamic heating conditions. The detail numerical analysis was documented by Bai [14]. The results are shown by solid curves in Figure 2. Considering the fact that the temperature ranges of 400 to 475 °K covered by isothermal experiments [4], as represented by Eqs. (5.1) and (5.2), is narrower than the range of 320 to 600 °K covered here by the dynamic heating experiments, the agreements shown in Figure 2 are rather satisfactory. The results also imply that information such as chemoviscosity $\eta(t)$ and degree of cure $\alpha(t)$ under dynamic heating cure conditions can be related, within certain accuracy, to those obtained under isothermal curing conditions.

Determination of Glass Transition Temperatures

The temperature range in which chemoviscosity-time profiles become important in the processing for the resin system investigated here is 320 - 480°K, as will be shown subsequently. The range of degree of cure is roughly between 0 and 0.6. It is this range of α in which the relationship between $T_g(t)$ and $\alpha(t)$ needs to be determined.

The glass transition temperature, $T_g(t)$, was determined for isothermal curing conditions at five temperatures of 430, 440, 450, 460 and 480 °K, respectively. A set of three degree of cure was selected for each curing temperature. The corresponding set of curing time, t , was then determined by solving Eqs. (5.1) and (5.2) isothermally. For each DSC measurement under a given temperature, a fresh uncured sample was first cured in DSC for a period of time which was predetermined to yield the selected degree of cure α . At the completion of cure time, the sample was quenched to the room temperature, immediately followed by a second scan to determine the T_g of the cured sample. The results are tabulated in Table 2, where T_g s were determined at the inflection points on the thermograms. It is found that the value of T_g in isothermal curing condition depends not only on the degree of cure (or curing time), but also the curing temperature. A plot of T_g vs. α at various curing temperatures is given in Figure 3. Although T_g s are not expected to vary linearly with a over entire range of cure, it is noted that under each curing temperature, a linear relationship between T_g and α exists within certain range of α as indicated in Table 2. The relationship between $T_g(t)$ and $\alpha(t)$ can be expressed as

$$T_g(t) = A(T) \alpha(t) + B(T), \quad (6)$$

where the values of the temperature dependent parameters, $A(T)$ and $B(T)$, are tabulated in Table 3. Theoretically $B(T)$ is the glass transition temperature of the uncured resin, and should be a constant. The observed variations in $B(T)$ come from the extropolation of the linear representation of T_g vs. α by Eq. (6) to $\alpha=0$. For the chemoviscosity simulation under dynamic heating conditions reported below, only the appropriate range of α , by which Eq. (6) truly represents (see Table 2), is used. Arrhenius type of plots for $A(T)$ and $B(T)$ are shown in Figure 4. A constant value of $B = 289^\circ\text{K}$ is chosen for curing temperature below 455°K . By means of least square fit the straight lines can be represented, respectively, by

$$\begin{aligned} \text{Log } A(T) &= -667.43/T + 3.421, & T \leq 455^\circ\text{K} \\ \text{Log } B(T) &= 2.461, \end{aligned} \quad (7.1)$$

$$\begin{aligned} \text{Log } A(T) &= -3137.77/T + 8.913, & T > 455^\circ\text{K} \\ \text{Log } B(T) &= 444.15/T + 1.485. \end{aligned} \quad (7.2)$$

The correlation factors of the above linear fits are better than 0.99.

The glass transition temperatures for the material cured at a constant rate of heating condition of 20°K/min were also measured. Measurements were repeated for ten different samples. The results are tabulated in Table 4. For a given sample in these measurements, the temperature scan in DSC was started at 300°K. When it reached a predetermined temperature, T_p , the sample was quenched immediately to the room temperature, and followed by a second scan to determine the value of T_g . The predetermined temperature, T_p , defines a material state. Eight different material states (320, 400, 425, 450, 475, 500, 510 and 525°K) of the advancing material during curing were selected during each temperature scan from 320 to 525°K. The degree of cure at each material state calculated by the expanded Taylor series of Eqs. (5.1) and (5.2), as illustrated before, is also included in the Table. Average value of T_g at each material state and the corresponding standard deviation are also reported. It is noted that the standard deviations increase with the temperatures and a 90% confidence level can be achieved within $\pm 3\%$ of the experimentally determined values of T_g .

The average values of T_g , reported in Table 4, versus the degree of cure α are plotted in Figure 5. Also included in the figure is the calculated values (solid curve), which are based on Eqs. (5.1), (5.2), (6), (7.1) and (7.2). Favorable comparisons are seen for the changes of the glass transition temperature in the dynamic heating cycle below $\alpha = 0.4$, where the simulations of the chemoviscosity-time profiles become critical.

Chemoviscosity Modeling

Chemoviscosities for the material cured under isothermal conditions are shown in Figure 6. Seven isothermal curing conditions, ranging from 360 to 435 °K were selected. It is noted that for the higher curing temperatures, shorter curing times are required to reach the same viscosity level. At the initial stages of cure, lower levels of viscosity observed for the higher curing temperatures are attributed to the temperature effects. The nonlinearity existing among data in such a semi-logarithmic plot is apparent in the figure.

To model the chemoviscosity of the material under a given isothermal curing condition, the following set of equations is used:

$$\log \left(\frac{\eta_T}{\eta_{T_g}} \right) = - \frac{C_1 (T - T_g)}{C_2 + T - T_g} \quad (8.1)$$

$$T_g(t) = A(T_c) \alpha(t) + B(T_c), \quad (8.2)$$

and

$$t = \frac{a}{k_2} \ln \left(1 + \frac{k_2}{k_1} \alpha \right) - b \ln (1 - \alpha) - c \ln \left(1 - \frac{\alpha}{B} \right), \alpha \leq 0.3 \quad (8.3)$$

$$t = - \frac{1}{k_3} \ln \left(\frac{1 - \alpha}{0.7} \right) + t_c, \quad \alpha > 0.3 \quad (8.4)$$

where T_c is the isothermal curing temperature. Values of $A(T_c)$ and $B(T_c)$ in Eq. (8.2) are given by Eqs. (7.1) and (7.2). Eqs. (8.3) and (8.4), which describe explicitly the relationship between degree of cure, α , and the curing time, t , are obtained by integrating the kinetics model of Eqs. (5.1) and (5.2), which were reported by Lee et al. [4]. Expressions for the parameters a, b, c, t_c are also included in Table 1. t_c is the time given by Eq. (8.4) at $\alpha = 0.3$. In order to solve Eqs. (8) for the chemoviscosity η_T , the value of η_{T_g} remains to be specified. It is known that the viscosity at T_g varies with materials having different molecular weights. A common value of $\eta_{T_g} = 10^{12}$ Pa sec exists for high molecular weight liquids [15, 16]. Utracki and Ghijssels [17] reported the temperature dependence of the melt viscosity of net epoxy resins. The series of Epikote resins used in their study has values of T_g ranging from 258 to 352 K. This range of T_g is coincided with that exhibited by the material studied here. The viscosities of those Epikotes at T_g were found to increase with molecular weight, ranging from 1.6×10^8 to 3.0×10^{11} Pa sec. For the purpose of chemoviscosity modeling investigated here, a value of $\eta_{T_g} = 10^9$ Pa Sec is selected in the present study.

The comparisons between model predictions (solid curves) and experimental data are shown in Figure 7. Values of $C_1(T_c)$ and $C_2(T_c)$ determined for those seven cure temperatures are listed in Table 5. Very satisfactory comparisons are achieved. It is noted that a single set of C_1 and C_2 (i.e. not set of $C_1(t)$ and $C_2(t)$) is sufficient for each isothermal condition. Similar good matches between the experimental data and the model predictions are attainable for other choices of η_{T_g} . It is also noted that the model has more flexibilities over that of Eq. (1) in simulating the

nonlinear chemoviscosity-time profiles. Figure 7 can also be replotted as η vs. α shown in Figure 8, where values of α are obtained by solving Eqs. (8.3) and (8.4). Figure 8 shows that the viscosity level is very sensitive to the curing temperature. The gelation of this material, when the viscosity approaches infinity, seems to occur beyond $\alpha = 0.6$.

The temperature dependent C_1 and C_2 are plotted in Figure 9. The following expressions are found to describe these two parameters reasonably well:

For $T < 385$ °K

$$C_1 = 1.058 \times 10^5/T - 177.69, \quad (9.1)$$

$$C_2 = 900.$$

For $T > 385$ °K

$$C_1 = -1.252 \times 10^5/T + 422.87, \quad (9.2)$$

$$C_2 = -3.054 \times 10^6/T + 8767.46.$$

To model the chemoviscosity for the material cured under a dynamic heating cycle, similar techniques as those used in the isothermal cases are employed. The advancement of resin in terms of the degree of cure under dynamic heating conditions can be calculated from Eqs. (5.1) and (5.2) by means of the Taylor's series expansion as discussed above. By substituting Eqs. (6), (7.1), (7.2), (9.1) and (9.2) into Eqs. (8.1) and (8.2), the chemoviscosity-time profiles can therefore be simulated.

Values of $\alpha(t)$ determined by the Taylor's series expansion depend slightly on the time interval Δt chosen. Theoretically, $\alpha(t)$ can be determined more accurately when a smaller Δt is used. The effect of step size Δt on the calculated degree of cure $\alpha(t)$ is given in Table 6. The differences in $\alpha(t)$ are within 2% and are negligible. The step size of $\Delta t = 0.01$ minutes was chosen for all calculations.

Chemoviscosities of the material were measured at heating rates of 1.79, 2.70 and 4.11°K/min. All cure cycles were started at 300 °K. The results of the model predictions are

shown by solid curves in Figs. 10 to 12. It is seen that the model calculations correctly predict the curing times where minimum viscosities occur for all three cases. The poorer comparisons on the latter part of each curve, where viscosities start to rise are due to the fact that the present model is inadequate for $\alpha > 0.4$ as shown in Figure 5. Figure 13 shows the experimental chemoviscosity vs. curing temperature for the three heating cases. All data falls onto a single curve. More scatter of data is observed on a similar plot with η vs. α in Figure 14. This is because of uncertainties in the calculations of α . The value of α where gelation occurs is around $\alpha = 0.7$.

CONCLUSIONS

A new approach for simulating chemoviscosity of thermosetting resin has been formulated. The model is developed by modifying the well-established Williams-Landel-Ferry (WLF) theory in polymer rheology for thermoplastic materials. From this investigation, the following conclusions can be made:

1. The advancements of the degree of cure $\alpha(t)$ and the glass transition temperature $T_g(t)$ for a reactive resin system cured under isothermal conditions are found to be related to those occurring under dynamic heating cure conditions. Analytical expressions are formulated, and reasonably accurate comparisons between the experimental and the calculated values for both α and T_g are noted.
2. By introducing relations between the glass transition temperature $T_g(t)$ and the degree of cure $\alpha(t)$ for the resin system under cure, the WLF theory can be modified to account for the factor of reaction time. Thus the model proposed is capable of simulating viscosity profiles in various cure cycles.
3. A single set of material parameters C_1 and C_2 is found to describe adequately the advancement of material state under each isothermal condition. The model is capable of simulating nonlinear $\log \eta$ vs. t curves which are observed for many reactive resin systems cured under isothermal conditions. When the values of $C_1(T)$ and $C_2(T)$ are included in the model to predict the chemoviscosity profiles under dynamic curing conditions, calculated values compared favorably with the experimental data.

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Table 1. Values of the constants in Eqs. (5.1), (5.2), (8.3) and (8.4) for Hercules 3501-6 resin system cured under isothermal condition [4].

$$B = 0.47$$

$$A_1 = 2.101 \times 10^9 \text{ min}^{-1}$$

$$A_2 = -2.014 \times 10^9 \text{ min}^{-1}$$

$$A_3 = 1.960 \times 10^5 \text{ min}^{-1}$$

$$\Delta E_1 = 8.07 \times 10^4 \text{ J/mole}$$

$$\Delta E_2 = 7.78 \times 10^4 \text{ J/mole}$$

$$\Delta E_3 = 5.66 \times 10^4 \text{ J/mole}$$

$$a = k_2^2 (B-1) / d$$

$$b = (k_1 + k_2 B) / d$$

$$c = -(k_1 + k_2) / d$$

$$d = (k_1 + k_2) [k_2 B^2 + (k_1 - k_2) B - k_1]$$

Table 2. Glass transition temperatures measured for Hercules 3501-6 resin system cured at five isothermal conditions

Cure Temperature (°K)	Cure Time (min.)	Degree of Cure α	Glass Trans. Temp. (°K)
430	0.85	0.1	298.0
	2.53	0.2	304.25
	6.73	0.3	312.5
440	0.67	0.12	300.25
	1.82	0.22	306.25
	4.73	0.32	316.88
450	0.55	0.15	307.0
	1.47	0.25	315.05
	3.78	0.35	324.0
460	0.92	0.25	318.0
	2.48	0.35	329.5
	4.75	0.45	343.75
480	1.3	0.35	338.3
	2.37	0.45	361.75
	3.83	0.55	385.3

Table 3. Values of A(T) and B(T)

T(°K)	A(°K)	B(°K)
430	72.5	290.4
440	83.15	289.5
450	85.0	294.1
460	128.8	285.4
480	235.0	256.0

Table 4. Glass transition temperature measured during reaction advancement of Hercules 3501-6 resin system cured in DSC under a heating rate of 20 °K/min

$T_p(^{\circ}\text{K})$	320	400	425	450	475	500	510	525
Run #								
α	0	0.0001	0.03	0.11	0.23	0.399	0.49	0.645
1	284	288		310		356.7		425.3
2	285.3	288		310.6		352		430.7
3	283.3	287.3		306.7		364		426
4	283.3	286		309.3		353		411.3
5	282.6			304.7		348.7		418
6	285.3		294		324		382	
7	284.3		294.7		328		378	
8	284.7		298.7		320.7		378	
9	283.3		295.3		323.3		371.3	
10	283.3		292		321.3		380.7	
Average $T_g (^{\circ}\text{K})$	283.94	287.33	294.9	308.3	323.47	354.88	378	422.26
Standard Dev. σ	0.934	0.943	2.442	2.485	2.002	3.899	4.129	6.318

Table 5. Values of C_1 and C_2 determined for the Hercules 3501-6 resin system cured under seven isothermal conditions

T_c ($^{\circ}\text{K}$)	C_1	C_2
360	117.0	900
375	102.5	900
385	98.3	900
399	110.5	1100
410	112.5	1200
425	134.5	1600
435	132.5	1800

Table 6. The calculated degree of cure $\alpha(t)$ by different time step size Δt (minutes)

Curing Time (min)	$\Delta t = 0.01$	$\Delta t = 0.05$	$\Delta t = 0.1$
6	.150226	.153258	.157127
8	.347579	.351781	.357062
10	.606030	.611808	.619061
12	.899822	.904560	.910432

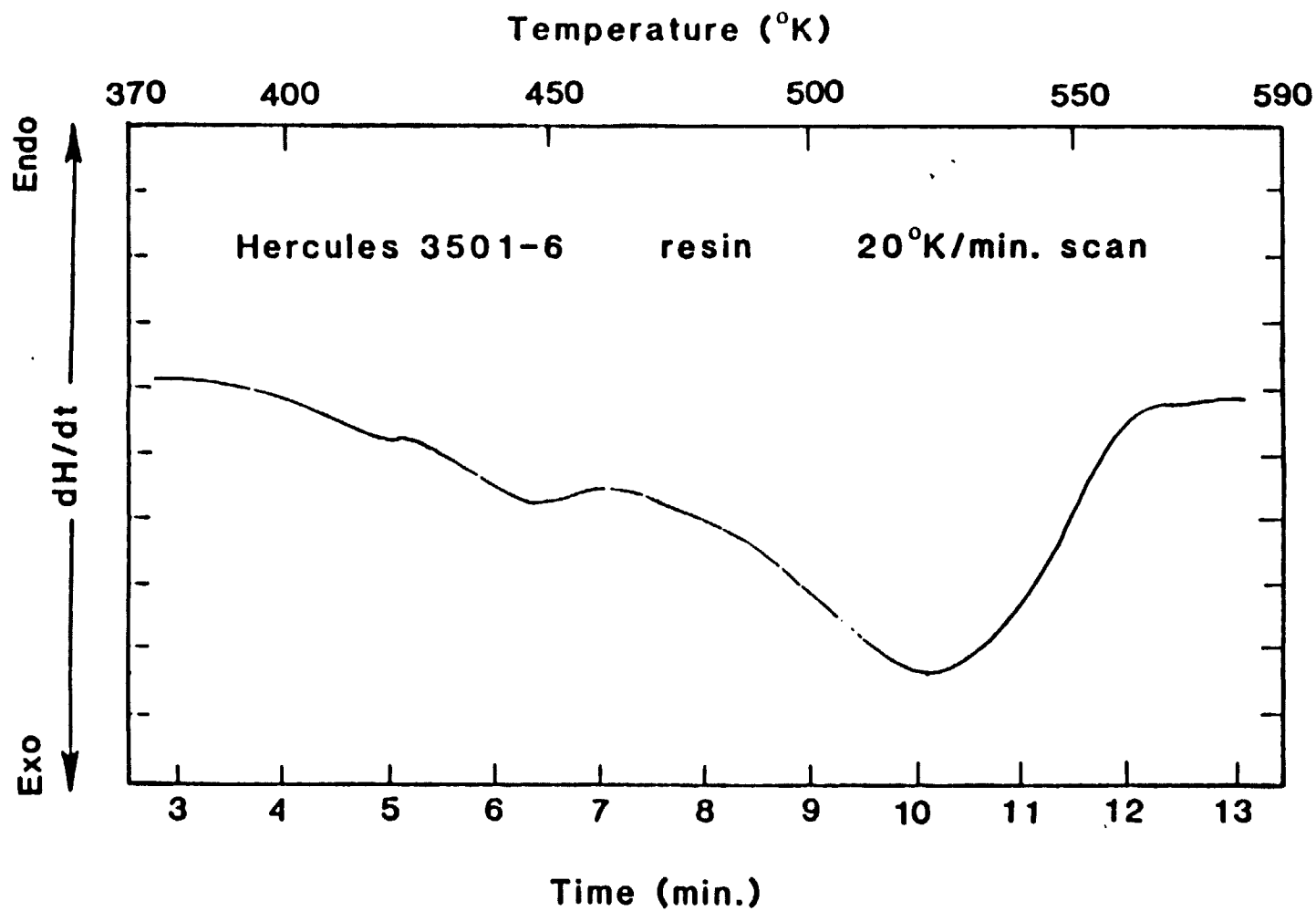


Fig. 1. DSC thermogram for the Hercules 3501-6 neat resin system undergoing a dynamic temperature scan of 20 $^{\circ}\text{K}/\text{min.}$

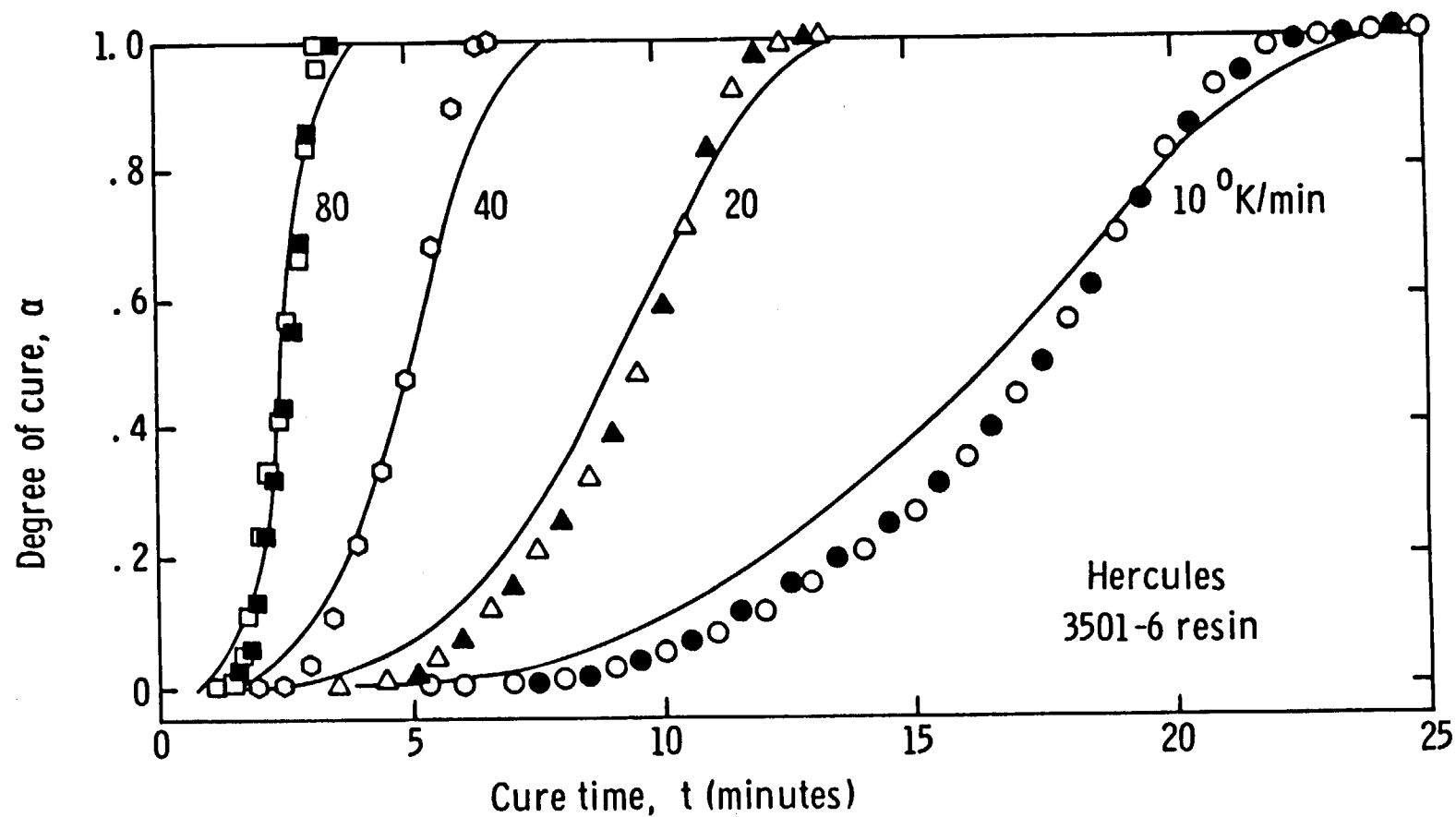


Fig. 2. Degree of cure versus cure time for samples cured at four different heating rates. Symbols are experimental data by DSC. Filled and open symbols of the same type represent duplicate runs. Solid curves are theoretical predictions based on the kinetics model of Lee et al. [4].

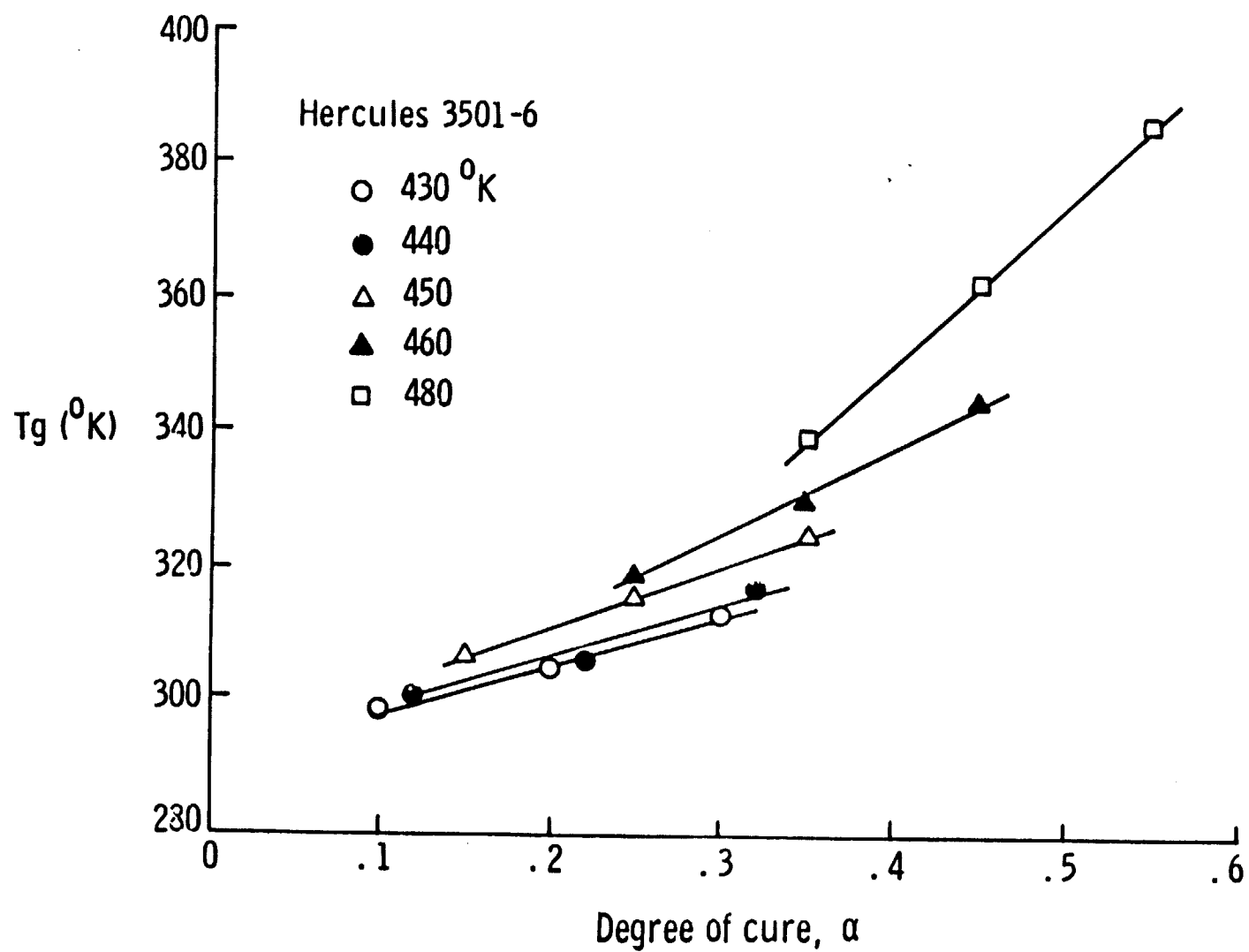


Fig. 3. The glass transition temperature, T_g , versus the degree of cure for samples cured at five isothermal conditions.

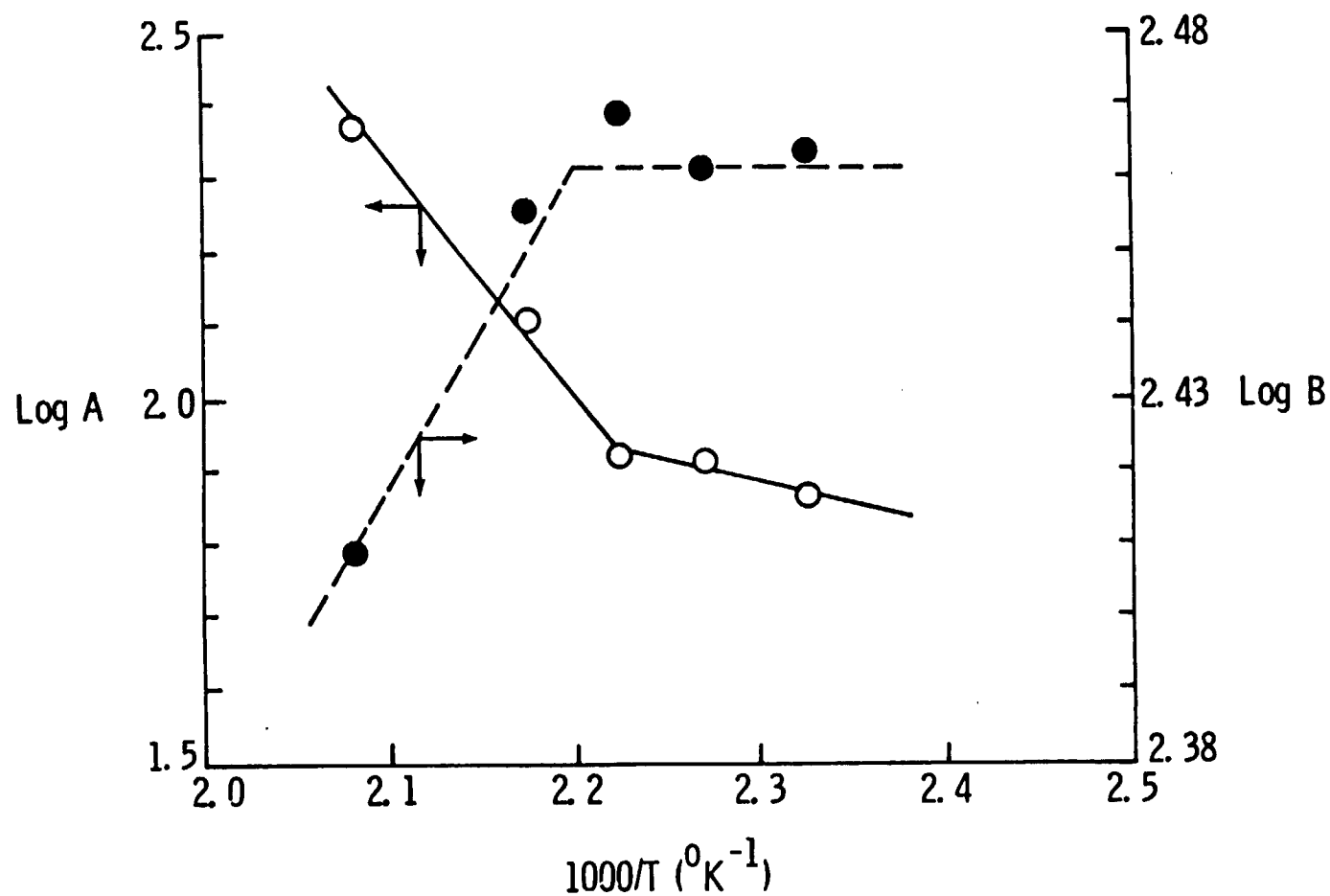


Fig. 4. Arrhenius relationships for the parameters A and B.

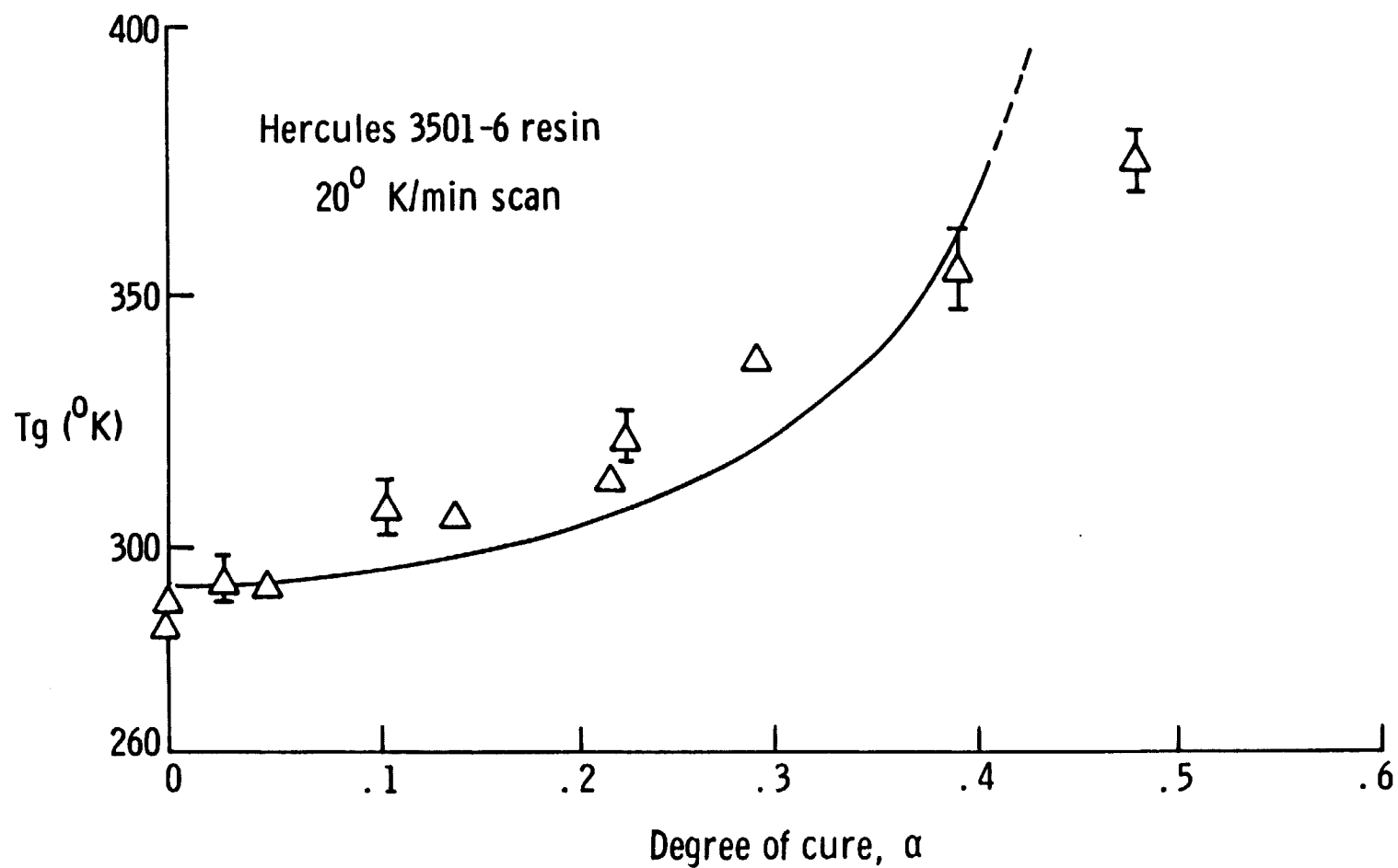


Fig. 5. The glass transition temperature, T_g , versus the degree of cure for samples cured under a dynamic temperature scan of 20 $^{\circ}\text{K./min}$. Symbols are experimental data. Solid curve is the theoretical calculation.

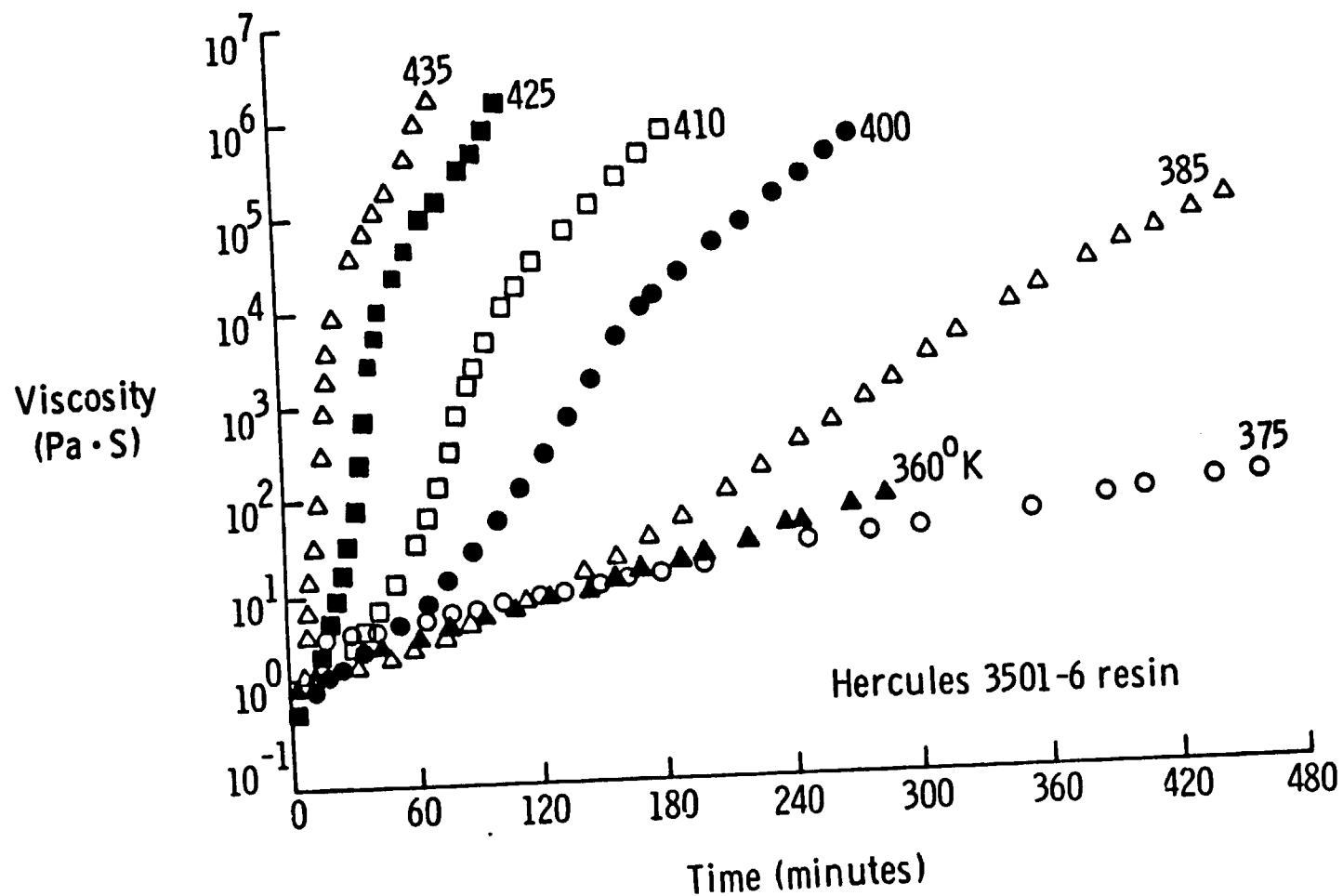


Fig. 6. Complex viscosity versus cure time for samples cured at seven different isothermal conditions.

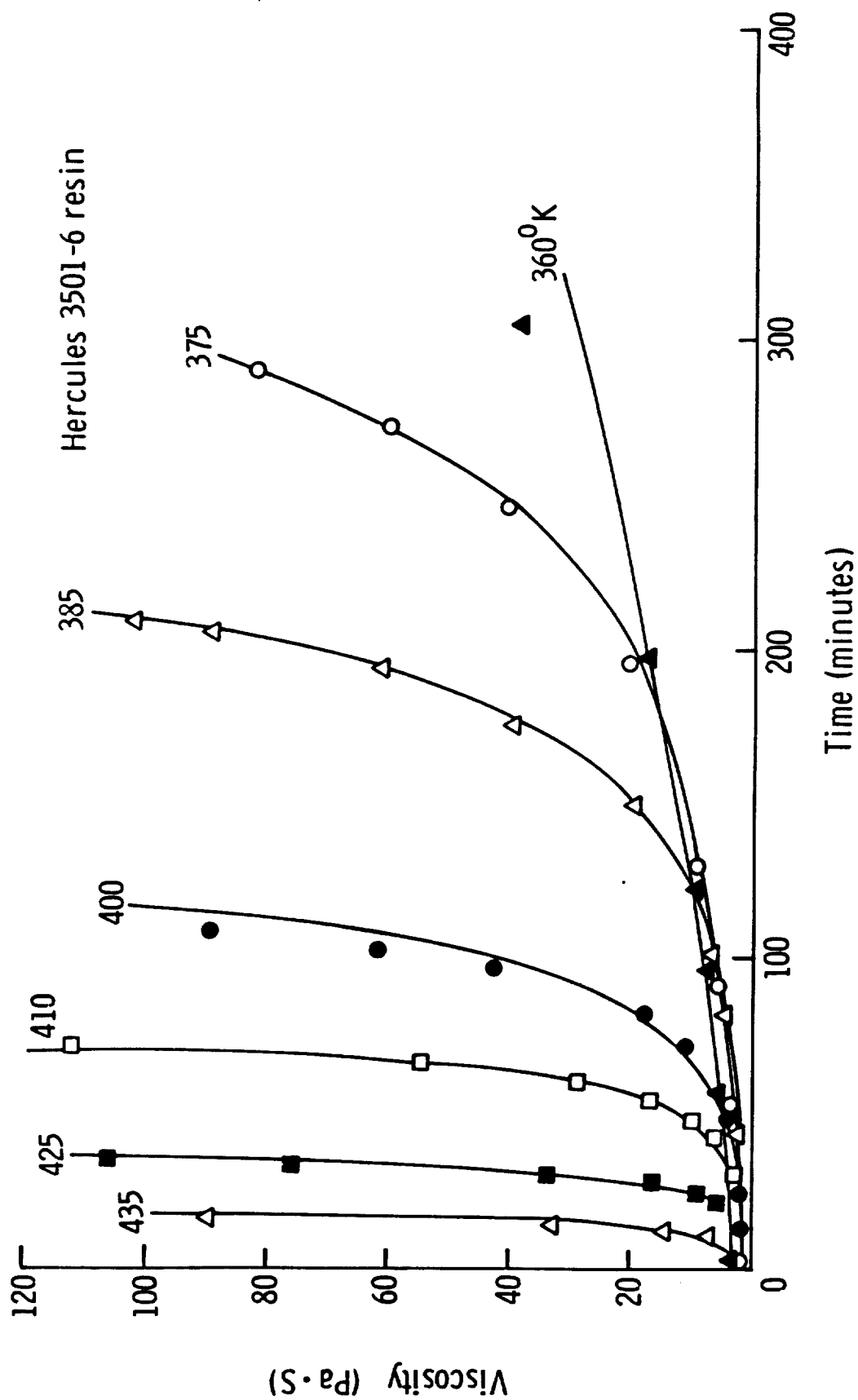


Fig. 7. Complex viscosity versus cure time for samples cured at seven different isothermal conditions. Symbols are experimental data by the Rheometrics System 4. Solid curves are theoretical calculations by Eqs. (8).

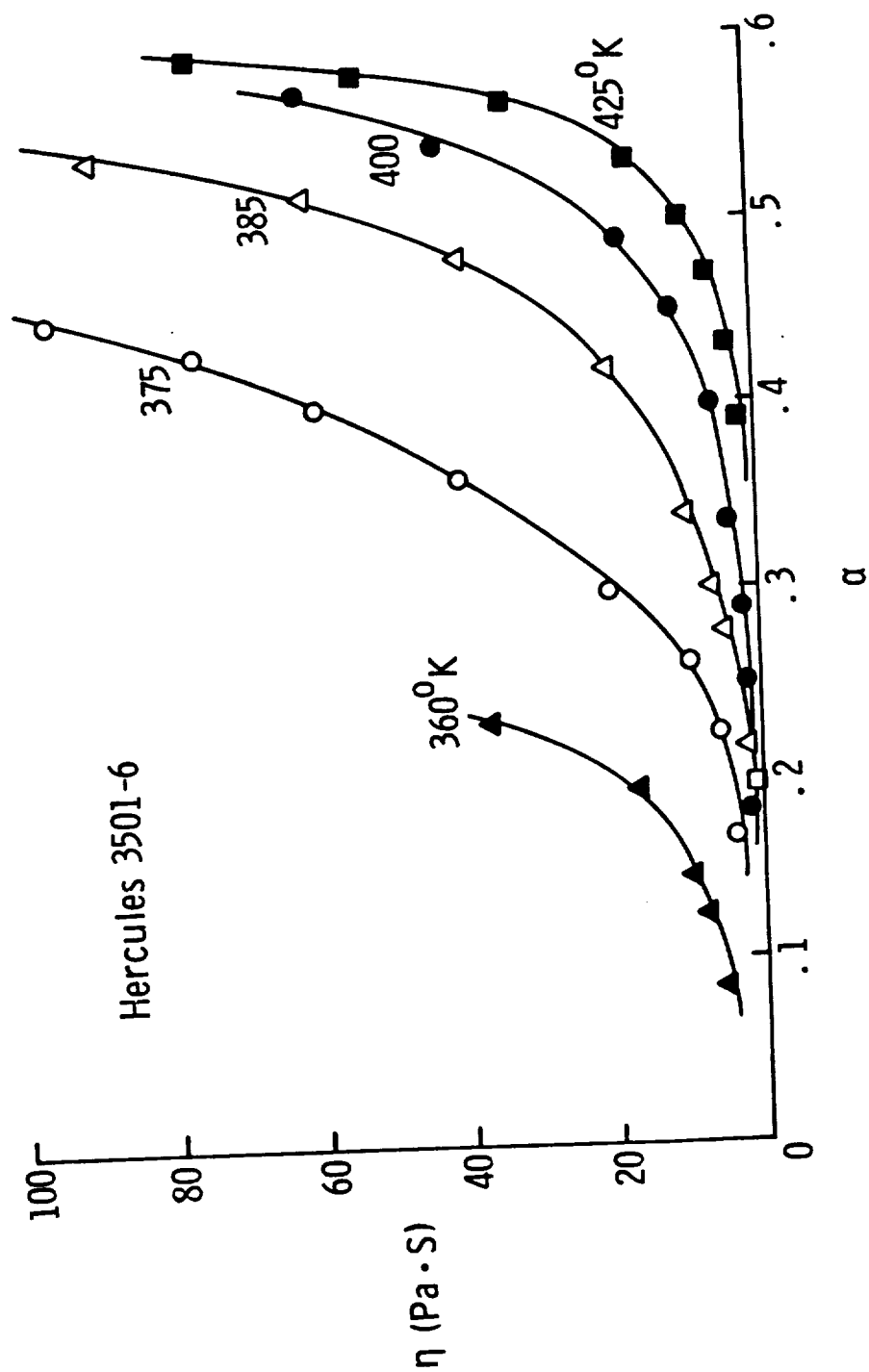


Fig. 8. Complex viscosity versus degree of cure for samples at five isothermal curing conditions. The degree of cure were calculated from Eqs. (8.3) and (8.4).

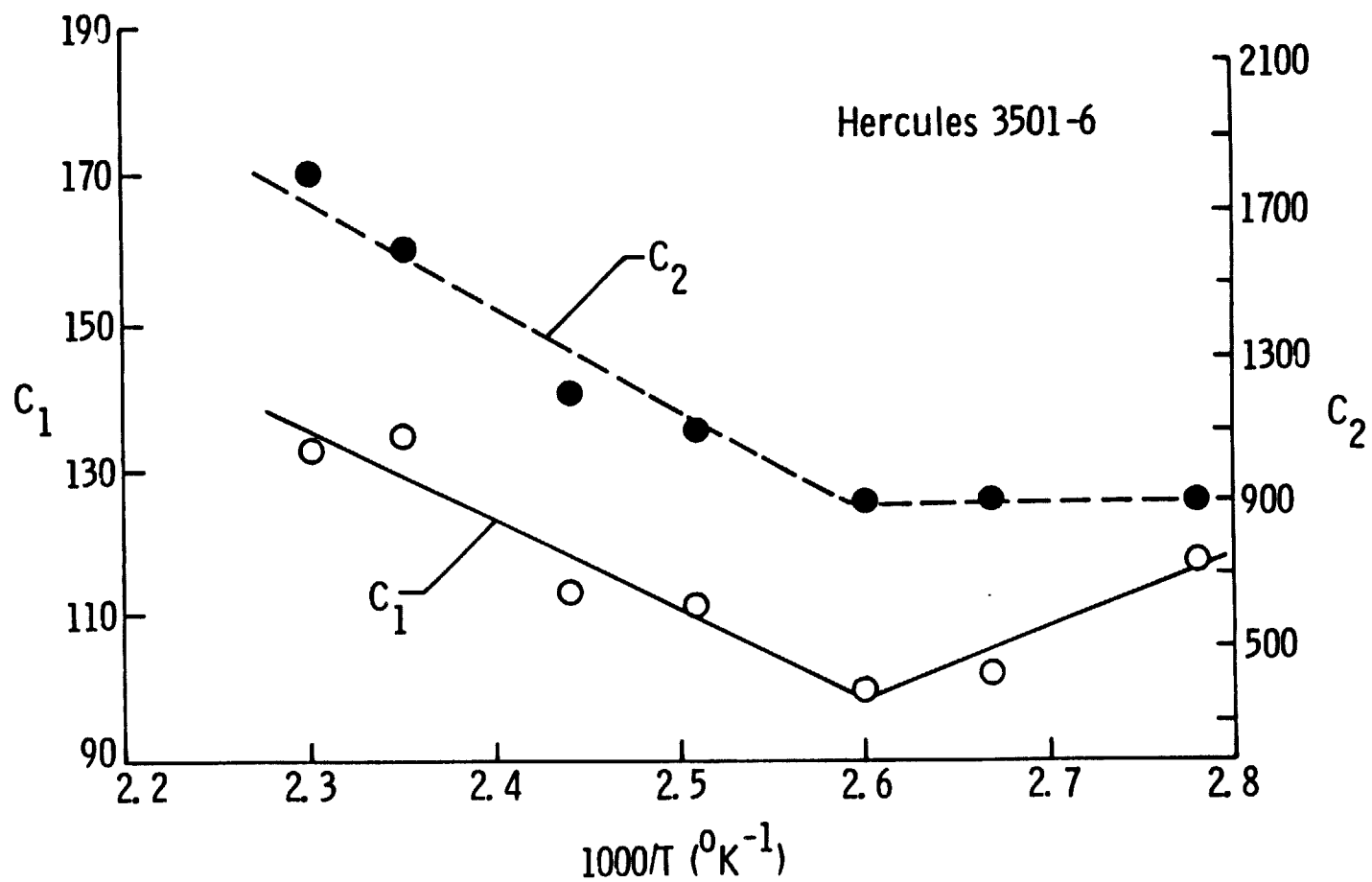


Fig. 9. Temperature dependences of the two material parameters C_1 and C_2 in the WLF equation for the Hercules 3501-6 resin system.

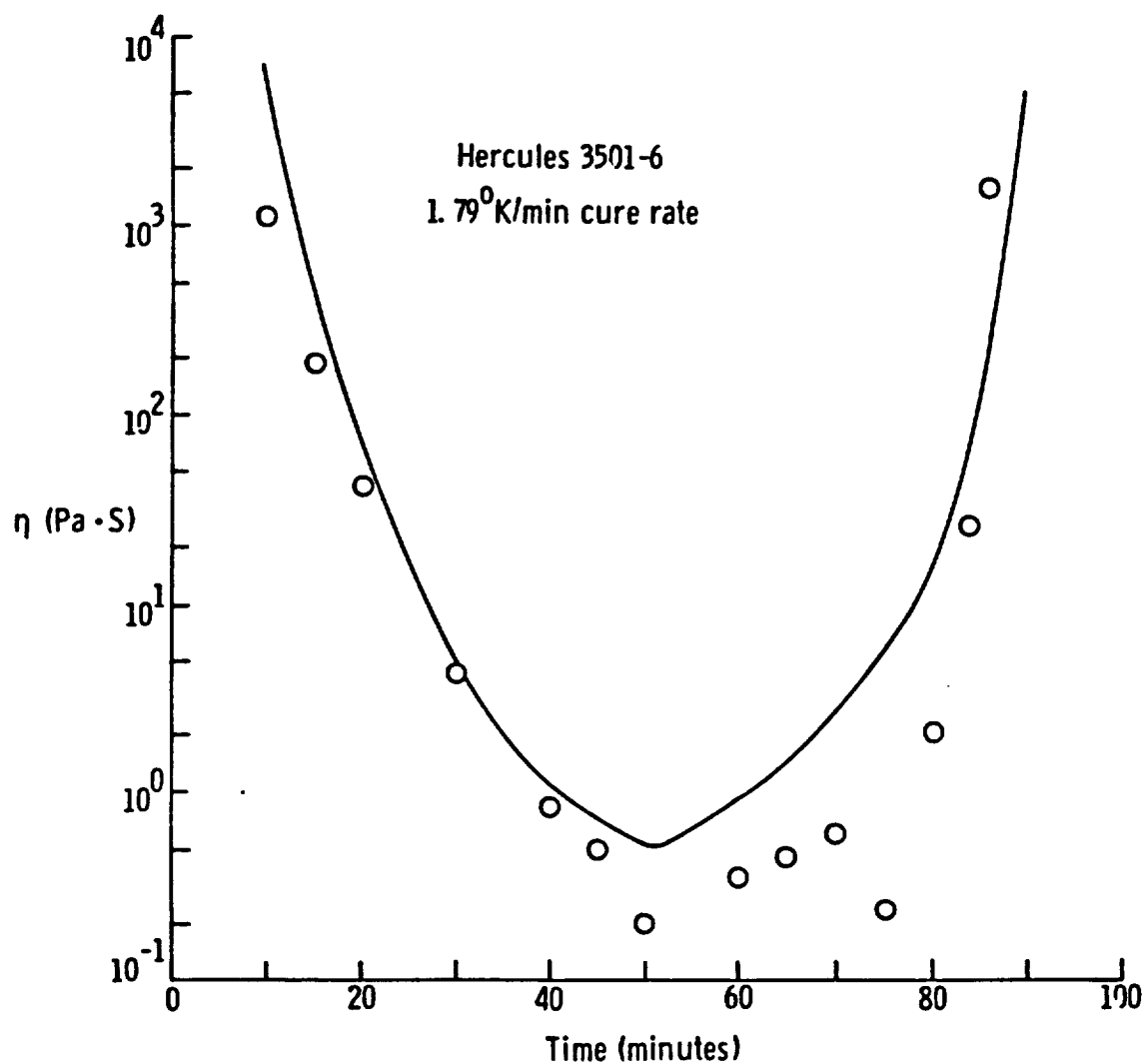


Fig. 10. Complex viscosity versus cure time for the sample cured under a dynamic temperature scan of 1.79 °K./min. Symbols are experimental data. Solid curve is theoretical prediction.

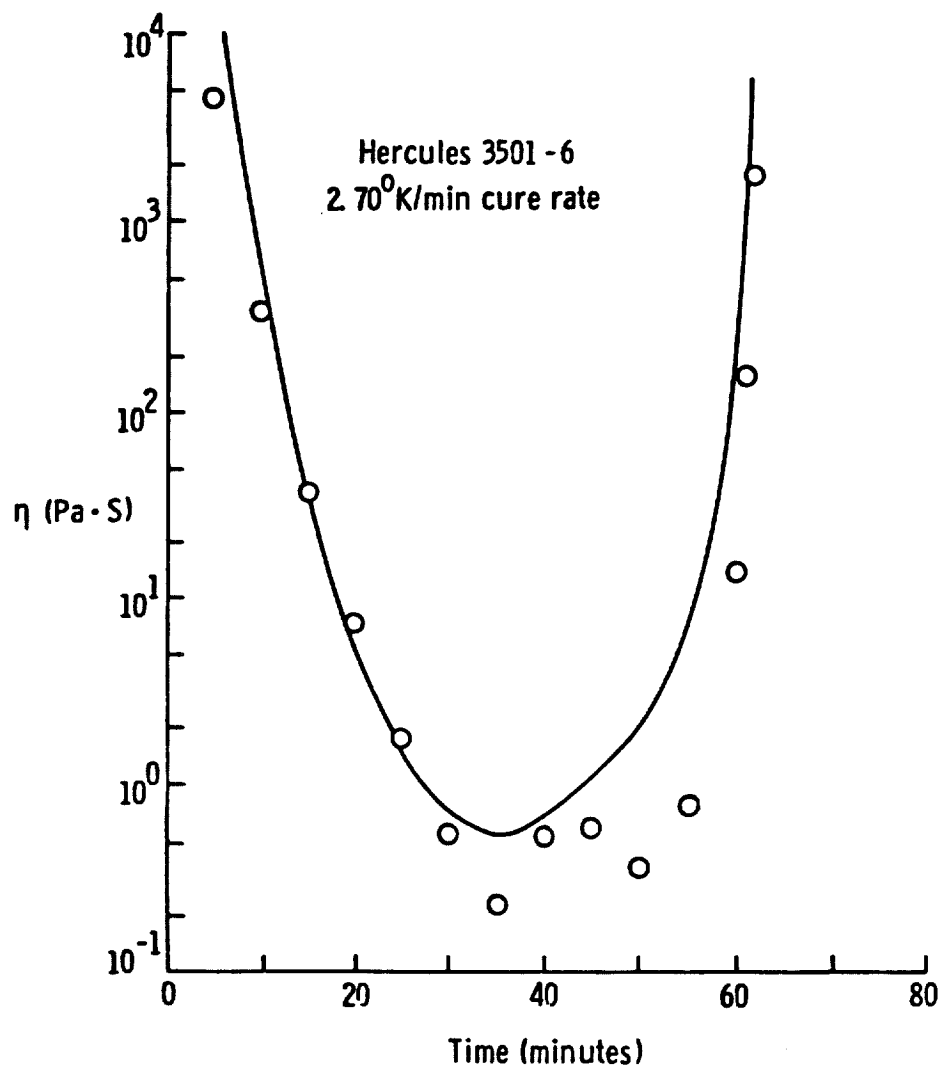


Fig. 11. Complex viscosity versus cure time for the sample cured under a dynamic temperature scan of 2.70 °K./min. Symbols are experimental data. Solid curve is theoretical prediction.

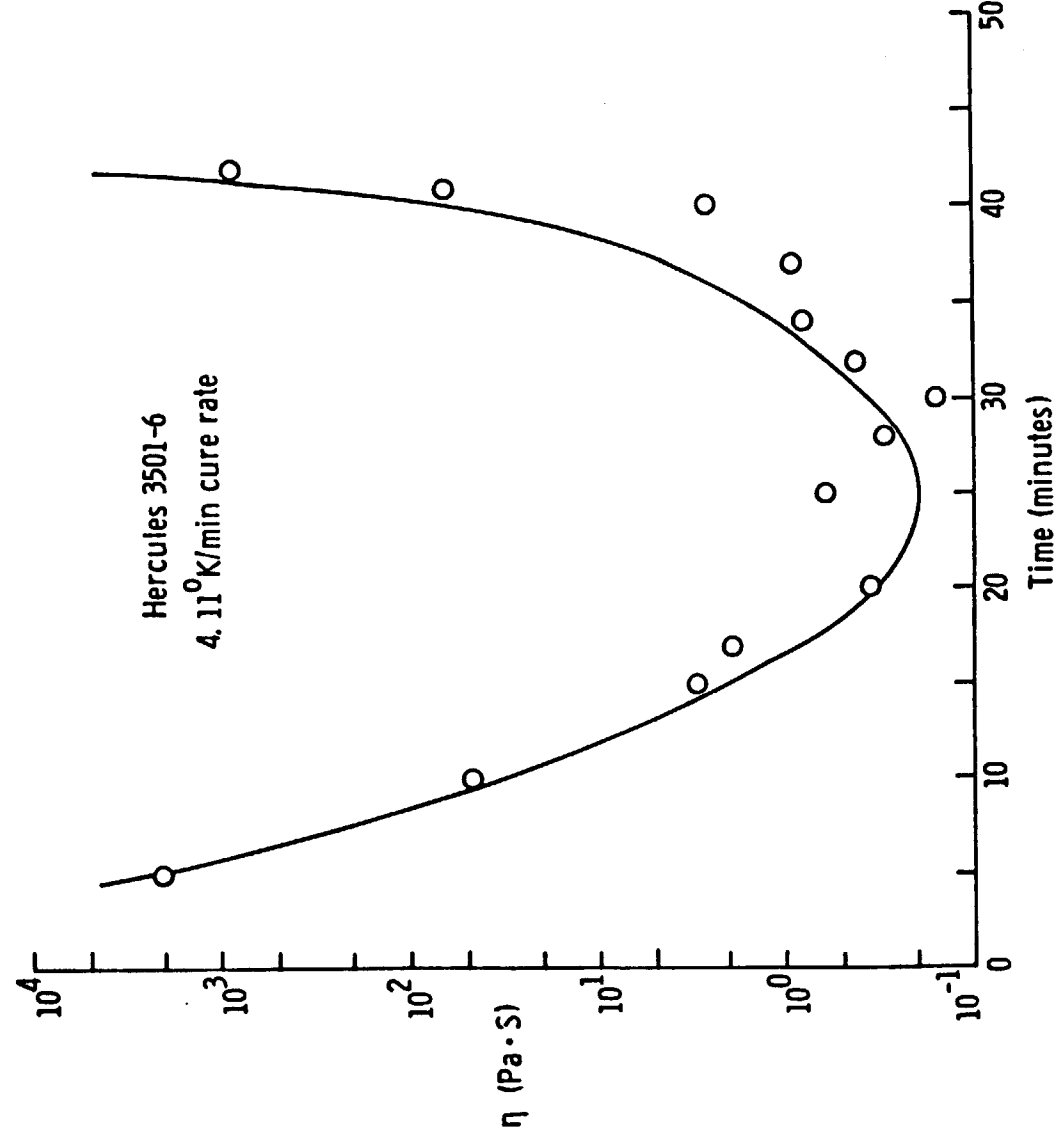


Fig. 12. Complex viscosity versus cure time for the sample cured under a dynamic temperature scan of 4.11 °K./min. Symbols are experimental data. Solid curve is theoretical prediction.

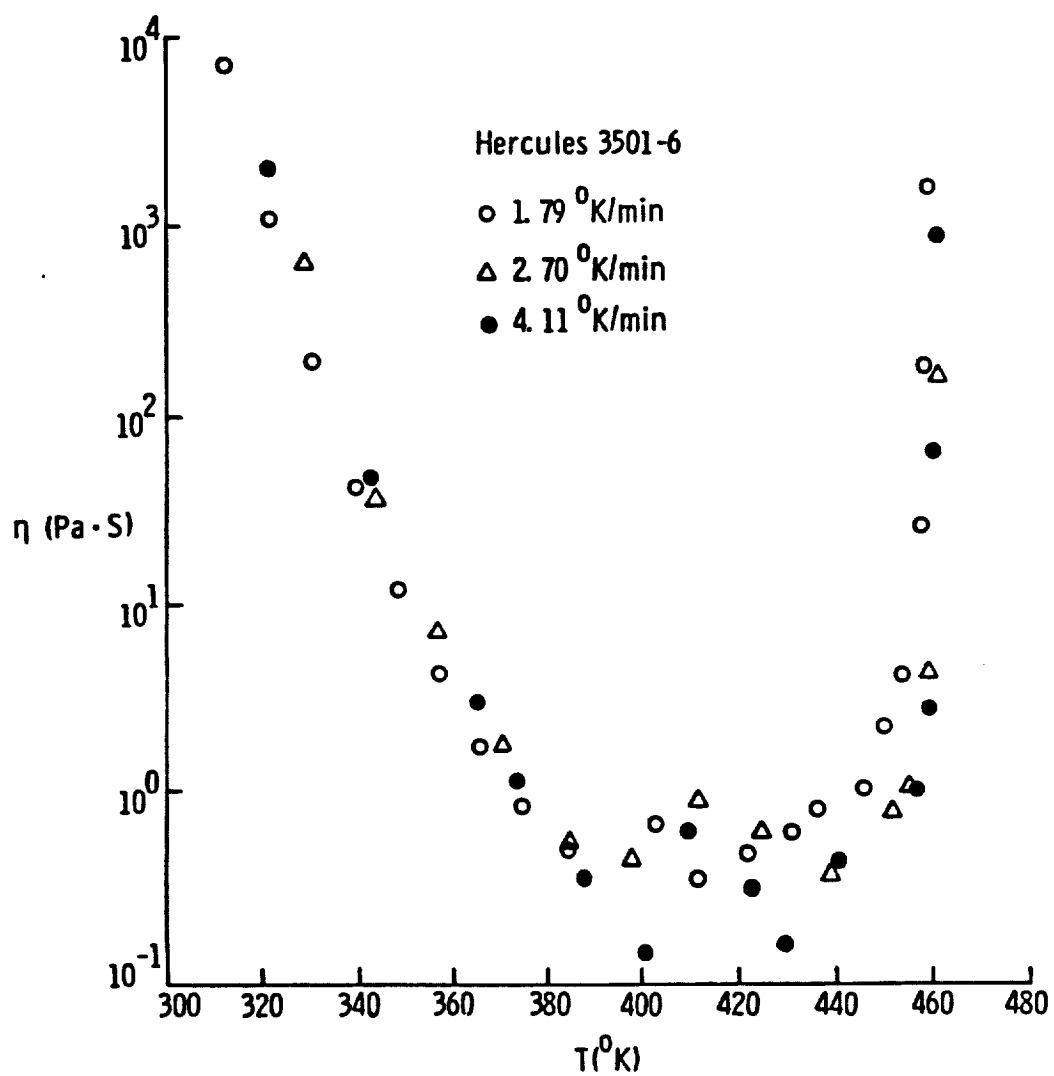


Fig. 13. Complex viscosity versus curing temperature for samples cured at three different heating rates indicated.

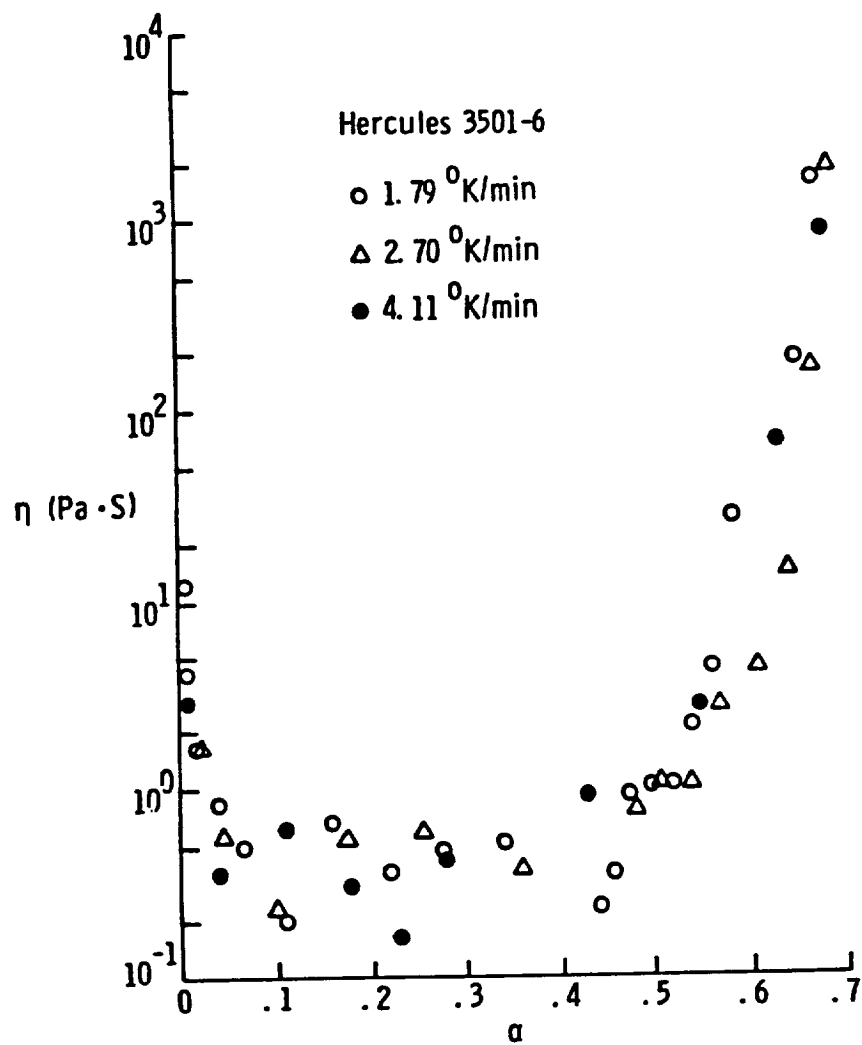


Fig. 14. Complex viscosity versus degree of cure for samples cured at three different heating rates indicated.



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16. Abstract A new analytical model for simulating chemoviscosity of thermosetting resin has been formulated. The model is developed by modifying the well established Williams-Landel-Ferry (WLF) theory in polymer rheology for the thermoplastic materials. By introducing a relationship between the glass transition temperature $T_g(t)$ and the degree of cure $\alpha(t)$ of the resin system under cure, the WLF theory can be modified to account for the factor of reaction time. Temperature-dependent functions of the modified WLF theory parameters $C_1(T)$ and $C_2(T)$ were determined from the isothermal cure data. Theoretical predictions of the model for the resin under dynamic heating cure cycles were shown to compare favorably with the experimental data. This work represents a progress toward establishing a chemoviscosity model which is capable of not only describing viscosity profiles accurately under various cure cycles, but also correlating viscosity data to the changes of physical properties associated with the structural transformations of the thermosetting resin systems during cure.					
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